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RESEARCHES
ON THE
DOUBLE HALIDES.

A DISSERTATION

PRESENTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS
UNIVERSITY FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

BY

CHARLES E. SAUNDERS.

1891.

BALTIMORE:
PRESS OF ISAAC FRIEDENWALD CO.
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The present investigation was carried out under the direct supervision of Prof. Ira Remsen, to whom the author wishes to express his sincere gratitude for the instruction received.

The writer would also express his thanks to Dr. G. H. Williams for assistance in the crystallographic part of the work.

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INTRODUCTION.

The investigation, an account of which is here given, bears on the general questions as to the structure and the conditions of formation of the double halides. Compounds of this class, though known for many years, did not, until recently, attract much attention. Being regarded as *molecular* and not *atomic* compounds, the investigation of their structure seemed to present unusual difficulties. The apparent analogies between the double halides and the oxygen salts were frequently discussed,¹ but it was not until 1867 that the conception of the union of the molecules through the chlorine atoms was first put forward by Naquet.² This theory has since been expressed by several other chemists,³ and was recently fully discussed by Professor Remsen,⁴ who laid special stress on the view that pairs of halogen atoms exert a linking function in these compounds similar to that exerted by single oxygen atoms in the oxygen salts, and formulated the following law in regard to the composition of the double halides:

"When a halide of any element combines with a halide of an alkali metal to form a double salt, the number of molecules of the alkali salt which are added to one molecule of the other halide is never greater and is generally less than the number of halogen atoms contained in the latter."

This law was based on the formulas of several hundred double halides; nevertheless, a few exceptions to it are found recorded in chemical literature. Some of these records have already been shown to be incorrect.

The present paper treats in the first part of some of the double halides containing manganese, and in the second chiefly of some of the supposed exceptions to the law stated above.

¹ Von Bonsdorff, Ann. chim. phys. [2] 34, 142; Boullay, Ibid. [2] 34, 337; Bolley, Liebig's Ann. 39, 100; Liebig, Ann. chim. phys. [2] 35, 68; Berzelius, Berz. Jahrb. 8, 138.

² Principes de Chimie fondée sur les Theories Modernes, Paris, 1867, p. 62.

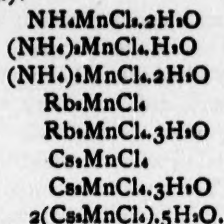
³ See especially Blomstrand, Die Chemie der Jetztzeit etc., Heidelberg, 1869; Armstrong, British Assoc. Reports, 1885, 959; Heyes, Phil. Mag. 25, 221, 297.

⁴ Am. Chem. Jour. 11, 291.

PART I.

MANGANESE COMPOUNDS.

The following is a list of the salts hitherto described containing manganous chloride, combined with the chloride of some alkali metal (or of ammonium):



Each of the salts in this very irregular series will be considered in detail in its proper connection. There is, however, a salt which should be considered before taking up the compounds in this list and those closely related to them.

Manganous Chloride, $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$.

In attempting to prepare a double chloride of manganese and lithium, and also of manganese and magnesium, a substance was obtained which proved to be manganous chloride with two molecules of water of crystallisation instead of four, which is the normal number. The new form of the substance was obtained by adding a considerable quantity of ordinary manganous chloride to a concentrated solution of lithium chloride in water, then evaporating somewhat and allowing to cool. When magnesium chloride was used instead of lithium chloride, either alcohol containing water, or water alone served as the solvent, a few drops of hydrochloric acid being usually added. When magnesium chloride is present there must be added a considerable excess of manganous chloride, or a double salt will be produced instead of the simple chloride. Manganous chloride, as thus obtained, crystallised in beautiful pink crystals, usually about one centimeter in length and quite slender. The ends of the crystals were frequently hollow for some distance inward. They usually formed radiating groups, but were sometimes obtained in perfectly definite crossed twins.

The substance acts in general like ordinary manganous chloride, except that, as would be expected, it does not lose water of crystallisation when dried over calcium chloride, while the ordinary form loses two of its four molecules under these conditions. Analysis showed that the same salt was obtained from a solution containing lithium chloride as from one containing magnesium chloride. From the conditions of formation a pure product could not, however, be expected. The analyses here given were made first with a sample which had been dried between filtering paper, and, second, with one dried to constant weight over calcium chloride.

Analysis of salt dried between filtering paper gave the following results:

0.3924 gram salt gave 0.6753 gram AgCl (42.56 per cent. Cl), and 0.1788 gram Mn_2O_3 (32.82 per cent. Mn).

When dried over calcium chloride the salt gave the following figures on analysis:

0.3346 gram salt gave 0.5902 gram AgCl (43.62 per cent. Cl), and 0.1581 gram Mn_2O_3 (34.03 per cent. Mn).

0.2975 gram lost at 105° – 110° 0.0326 gram H_2O = 10.96 per cent. H_2O .

At higher temperatures further, but slow, loss was observed, no doubt due to decomposition of the salt.



	Calculated for $MnCl_{1.2}H_2O$.		Found	
			In dried salt.	In undried salt.
Mn	54.8	33.94	34.03	32.82
2Cl	70.74	43.81	43.62	42.56
H_2O	17.96	11.125	10.96	
H_2O	17.96	11.125		
	161.46	100.000		

It is evident, therefore, that the salt has the formula $MnCl_{1.2}H_2O$, and loses one molecule of water at 105° .

Crystallography of the salt.—It crystallises in slender prisms (Fig. 1), which were shown by their optical properties and angular measurements to be monoclinic. The crystals were usually hollow towards the end, so that the basal plane was very imperfectly developed.

On this account the crystallographic angle β was found (roughly) by measurement on a petrographical microscope, the crystal

FIG. 1.

resting on one of the clinopinacoids. The other angle was measured on a Fuess goniometer. The forms observed were :

$$c = \infty P, [001].$$

$$m = \infty P, [110].$$

$$b = \infty P \bar{c}, [010].$$

The angles measured were : $m : m = 100^\circ 45'$, and $\angle \beta = 42^\circ$ (nearly). From these data, taking $\bar{b}$ as unity, we have $\bar{a} = 1.238$ (nearly).

The substance sometimes forms crossed twins in which the basal plane is the twinning plane. An orthographic projection of such a twin is shown in Fig. 2.

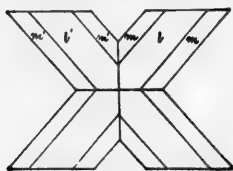


FIG. 2.

It seems probable that the magnesium chloride, or lithium chloride, present when manganous chloride crystallises out with only two molecules of water must act as a sort of dehydrating agent; and it is not unlikely that the presence of such salts as these in solutions in other cases would lead to the formation of crystals of various substances, containing less than their normal number of molecules of water.

Experiments with Potassium Chloride, etc.

On adding potassium chloride to a hot aqueous solution of manganous chloride, sufficiently concentrated to deposit crystals on cooling, a considerable amount of the alkali chloride is dissolved. When the solution cools crystals of a double chloride are deposited, which are pale pink in color, and usually form radiating groups. The individual crystals are elongated and very thin as produced in this way; but by spontaneous evaporation of the solution they can be obtained in much larger form. They are very soluble in water, but cannot be recrystallised in the ordinary sense of the term, for their solution gives a deposit of potassium chloride only, until the manganous chloride is present in large excess. This decomposition of the salt occurs in the same way in the presence of hydrochloric acid, and seems to depend merely on the different solubilities of the two constituents.

The salt is deliquescent in moist air, and was therefore dried in a desiccator over calcium chloride before analysing. It seems to

retain its water of crystallisation under these conditions, though a slow loss in weight continues, probably due to the giving up of two molecules of water of crystallisation by the manganous chloride mechanically mixed with the salt. The presence of this manganous chloride accounts for the lack of agreement between the percentage composition found and that calculated. As manganous chloride retains one molecule of water at 110° , the analysis of the salt could not be expected to give figures adding up quite to 100 per cent.

The method used for the determination of the potassium and manganese was as follows: The manganese was precipitated as carbonate by means of ammonium carbonate and then burned to manganous-manganic oxide, while the filtrate was evaporated and the potassium weighed as chloride, after subliming off the ammonium chloride. The same method was used in the case of the rubidium and caesium salts. Here it has the great advantage of giving the alkali metal back again in the desired form. The precipitation of manganese by ammonium carbonate was found to be almost absolutely complete. Where the filtrate containing the alkali chloride was evaporated in glass vessels, a blank experiment, performed under similar conditions, gave the amount of glass dissolved, which was then deducted.

0.4562 gram salt gave 0.1479 gram Mn_2O_3 (23.35 per cent. Mn), and 0.1415 gram KCl (16.27 per cent. K).

0.2969 gram salt gave 0.5388 gram AgCl (44.88 per cent. Cl).

0.2517 gram salt lost at 105° – 110° 0.0381 gram H_2O = 15.14 per cent. H_2O .

	Calculated.		Found.
K	39.03	16.55	16.27
3Cl	106.11	44.99	44.88
Mn	54.8	23.23	23.35
2H ₂ O	35.92	15.23	15.14
	235.86	100.00	99.64

The salt has therefore the formula $KMnCl_3 \cdot 2H_2O$. It has not been previously described. All efforts to obtain a salt containing a larger proportion of potassium chloride failed. No iodide or fluoride of manganese and potassium was obtained, nor was a bromide obtained by itself, though the substance described below may be regarded as containing a simple double bromide.

Efforts were made to produce, if possible, mixed salts (a chlor-bromide and a chlor-iodide) of definite composition. These experiments will now be described.

If a hot, saturated solution of manganous chloride be saturated with potassium bromide and then allowed to cool, crystals are deposited exactly similar in appearance to those of the salt $\text{KMnCl}_2 \cdot 2\text{H}_2\text{O}$, but containing a considerable amount of bromine. On evaporation of the solution further deposits of crystals can be obtained. The percentage of bromine was found to vary in different crystallisations, as shown by the following analyses, the first being of a very early deposit and the second of a much later one:

I. 0.7380 gram of the salt was dissolved in 500 cc. of water and divided into two equal parts. In each portion the chlorine was precipitated as silver chloride, one of the precipitates being collected and weighed in a Gooch crucible, while the other was reduced to metallic silver in a current of hydrogen.

0.3690 gram gave 0.6621 gram $\text{AgCl} + \text{AgBr}$, and 0.4823 gram Ag. Hence $\text{Br} = 0.03836$ gram $= 10.40$ per cent., and $\text{Cl} = 0.14144$ gram $= 38.33$ per cent.

II. The amount of silver which a given weight of the salt would precipitate was determined volumetrically (by Mohr's method), and, in a separate portion, the weight of the mixed precipitates formed from a given amount of the salt was determined. This method is more rapid than the one previously mentioned, but the results are probably less accurate.

0.3134 gram salt gave 0.5434 gram $\text{AgCl} + \text{AgBr}$, and 0.3238 gram precipitated 0.40001 gram Ag. Hence $\text{Br} = 0.0521$ gram in 0.3134 gram salt $= 16.62$ per cent., and $\text{Cl} = 0.1041$ gram in 0.3134 gram salt $= 33.22$ per cent.

III. A complete analysis was made of a deposit intermediate between the two just given.

0.4719 gram lost at $105^\circ\text{--}110^\circ$ 0.0671 gram $\text{H}_2\text{O} = 14.22$ per cent. H_2O , and gave 0.1564 gram K_2SO_4 (14.88 per cent. K), and 0.1395 gram Mn_2O_3 (21.29 per cent. Mn).

0.3426 gram gave 0.5966 gram $\text{AgBr} + \text{AgCl}$, and 0.3133 gram precipitated 0.3916 gram Ag. Hence $\text{Br} = 14.53$ per cent., and $\text{Cl} = 34.62$ per cent. In this case the potassium was weighed as sulphate, to ensure the absence of bromine.

The above analyses show that the substance obtained is not a definite compound, but, in all probability, an isomorphous mixture of two salts. It was found by calculation that the mixture might consist of 77.2 per cent. $\text{KMnCl}_3 \cdot 2\text{H}_2\text{O}$ with 22.8 per cent. $\text{KMnBr}_3 \cdot 2\text{H}_2\text{O}$, or, supposing the mixed salts to exist, of 48.05 per cent. $\text{KMnCl}_3 \cdot 2\text{H}_2\text{O}$ with 51.95 per cent. $\text{KMnCl}_3\text{Br} \cdot 2\text{H}_2\text{O}$.

	Calculated for both mixtures.	Found.
Cl	34.73	34.62
Br	14.78	14.53
Mn	21.32	21.29
K	15.19	14.88
H ₂ O	13.98	14.22
	100.00	99.54

As the substance comes out of a solution containing a large excess of manganous chloride, as well as some manganous bromide, the agreement between the calculated composition and that found can hardly be expected to be very close. The fact that the salt $\text{KMnBr}_3 \cdot 2\text{H}_2\text{O}$ was not obtained in the experiments with the pure bromides might be considered as an argument in favor of the belief that the constituent containing bromine in this mixture was really some *mixed* salt, such as $\text{KMnCl}_3\text{Br} \cdot 2\text{H}_2\text{O}$. However, the explanation that the presence of the salt $\text{KMnCl}_3 \cdot 2\text{H}_2\text{O}$ gives crystallising power to the salt $\text{KMnBr}_3 \cdot 2\text{H}_2\text{O}$, so that the two can form an isomorphous mixture, involves perhaps less speculation.

When potassium iodide was used instead of the bromide, in attempting to prepare a mixed salt, crystals of the same habit as before were obtained. A complete analysis of these was made, and the salt was found to contain an amount of iodine so small that it must be considered as a non-essential constituent, present merely by the adhering of a certain amount of mother-liquor. The salt is too easily soluble to admit of its being washed to any considerable extent. In no case was so much as 1 per cent. of iodine found. The salt was, in fact, $\text{KMnCl}_3 \cdot 2\text{H}_2\text{O}$.

These experiments are of interest as showing what large amounts of potassium bromide and iodide are converted into the chloride by being dissolved in a solution of manganous chloride. These crystallisations were all made in neutral solutions so as to avoid the complications, in interpreting the results, which the presence of even a small quantity of acid would have introduced.

On adding excess of potassium chloride to a warm, saturated solution of manganous bromide in water, filtering while hot, and allowing to cool, a deposit of crystals was obtained consisting largely of potassium bromide. The solution was then evaporated and each successive deposit of crystals removed until a point was at length reached where crystals similar to those of $\text{KMnCl}_2 \cdot 2\text{H}_2\text{O}$ were formed. They contained bromine and manganese, as well as potassium and chlorine. Analysis showed that they did not correspond in composition to any definite simple salt, but were a mixture (probably an isomorphous mixture) of two or more compounds. It is probable that this substance contained the same salts as that produced by adding potassium bromide to a solution of manganous chloride.

A similar experiment using manganous iodide instead of the bromide gave no satisfactory results, manganous iodide being rather too unstable for this work. It was not to be expected, however, that a double salt would be obtained in this experiment, because the composition of the salts already described seems to prove that both manganous chloride and potassium chloride are necessary constituents in every case. The experiments with manganous chloride and potassium iodide showed how readily the chlorine passed over from the manganese to the potassium, so that it does not seem probable that the reverse action would take place to any considerable extent; hence the solution, in the experiment just mentioned, would contain only a very small quantity of manganous chloride, and the formation of a double salt would not be possible.

Crystallography of the salt.—Accurate measurements of the crystals were found very difficult, owing to the softness of the salt and its tendency towards deliquescence. Sufficient information was obtained, however, from the optical properties and measurements of some angles to show that the crystals are triclinic. Individual crystals often show very irregular development. The drawing given (Fig. 3) is merely to show their general shape, as most commonly obtained. As *gliding* is very readily produced in this salt, a sample of it was sent to Prof. Otto Mügge, of the University of Münster, who has been for some time making a special study of that phenomenon. He has kindly undertaken an investigation of the compound.



FIG. 3.

Experiments with Ammonium Chloride.

Up to the present time there have been described three compounds of manganous chloride with ammonium chloride:

$\text{NH}_4\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$, described by Hautz,¹

$(\text{NH}_4)_2\text{MnCl}_4 \cdot \text{H}_2\text{O}$, described by Rammelsberg² and by Pickering,³

$(\text{NH}_4)_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$, described by v. Hauer.⁴

The directions given by Hautz for the preparation of the salt described by him are simple. A solution of manganous chloride and ammonium chloride, mixed in the proportions required by the formula NH_4MnCl_4 , is to be evaporated to crystallisation. These directions being followed, a salt was obtained, which was evidently the same as that described by Hautz. Analysis proved, however, that its formula was not $\text{NH}_4\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$, but $(\text{NH}_4)_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$, though the salt as thus produced was not very pure. A pure product was afterwards obtained by mixing the two chlorides in about the proportions mentioned by Hautz, and allowing the aqueous solution to evaporate spontaneously for several months over sulphuric acid. At intervals the deposits of crystals were removed. The fifth sample was found to be pure; the others contained an excess of ammonium chloride.

The analyses of the salt gave the following results:

0.3693 gram gave 0.7870 gram AgCl (52.70 per cent. Cl).

0.3557 gram gave 0.1008 gram Mn_2O_3 (20.41 per cent. Mn).

1.1389 gram lost at 110° 0.1529 gram H_2O = 13.43 per cent. H_2O .

0.3015 gram gave 0.04037 gram NH_3 = 13.39 per cent. NH_4 .

The determination of the water of crystallisation in this salt is of no value. The water is not given off readily, and the anhydrous salt undergoes slow decomposition at 110° . The figures given merely indicate, therefore, the point beyond which the loss of weight was very slow.

	Calculated for $(\text{NH}_4)_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$.		Found.
Mn	54.8	20.43	20.41
4Cl	141.48	52.75	52.70
2NH ₄	36.02	13.43	13.39
2H ₂ O	35.92	13.39	13.43
	268.22	100.00	99.93

¹ Liebig's Annalen 66, 285.

² Jour. Chem. Soc., 1879, 654.

³ Pogg. Ann. 94, 507.

⁴ Jour. für pr. Chem. 68, 436.

The salt usually forms radiating groups of short crystals. It is pale pink in color and of hard texture. It is easily soluble in water, but cannot be obtained very pure by recrystallisation, as it requires the presence of an excess of manganous chloride before it crystallises in quite pure condition. It is not deliquescent in the air, and does not give up its water of crystallisation in a desiccator.

Crystallography of the salt.—Well-developed, individual crystals are not often obtained, and when found, the faces are not, as a

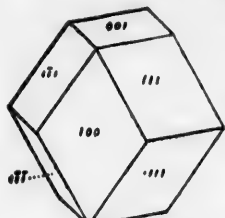


FIG. 4.

rule, bright enough for a satisfactory measurement of the angles with a goniometer. The salt (Fig. 4) is monoclinic in crystallisation, but possesses certain peculiarities due to the fact that two of its axes are almost (if not exactly) equal in length. While the values obtained for these axes are not identical, the difference is quite within the possible error caused by the imperfections of the crystal faces. Owing

to the habit of the crystals and the similarity in length of two of the axes, there is some resemblance between crystals of this salt and a rhombic dodecahedron. The cleavage is imperfect. The optical properties show that the crystals are monoclinic. The position of the *b* axis (the axis of symmetry) was determined by the extinction phenomena of the substance.

The forms observed were oP , $\infty P \infty$, $+P$ and $-P$.

Measurements obtained.	Angles calculated.
$III : \bar{III} = 121^\circ 36\frac{1}{2}'$	$121^\circ 37'$
$III : \bar{II}\bar{I} = 90^\circ 16\frac{1}{2}'$	$90^\circ 17'$
$II\bar{I} : \bar{III} = 95^\circ 42'$	$95^\circ 42'$
$III : 100 = 121^\circ 30'$	$121^\circ 29\frac{1}{2}'$
$III : II\bar{I} = 121^\circ 36\frac{1}{2}'$	$121^\circ 48'$
$II\bar{I} : 100 = 117^\circ 43'$	$116^\circ 53\frac{1}{2}'$
$001 : 100 = 95^\circ 25'$	$95^\circ 25'$
$III : 001$	$121^\circ 26\frac{1}{2}'$
$\bar{III} : 001$	$116^\circ 47\frac{1}{2}'$

These measurements were all made (except the last) from one crystal of the pure salt as used for analysis. The first four measurements were believed to be the best, and were therefore used in

calculating the lengths of the axes, and the angle β . They are probably correct within 5' or 6'. Those lower on the list were not believed to be as good. The constants found were:

$$\begin{aligned} a &= 1.4913 & b &= 1 \\ c &= 1.4956 & \angle \beta &= 84^\circ 35' \end{aligned}$$

Hautz describes the salt obtained by him as crystallising in the monoclinic system. The symbols he gives for the forms observed appear to mean that the crystals consisted of a prism, ortho and clino domes, with perhaps one of the pinacoids poorly developed. The symbol of the latter is enclosed in a parenthesis, and it is not clear to which pinacoid it refers. Now, by placing the crystals obtained in this investigation in an incorrect position the forms would become the same as those given by Hautz, except that no plane corresponding to his undetermined pinacoid was observed. The evidence is therefore pretty clear that the two salts are identical. The analyses of Hautz show that the substance as obtained by him was very impure, whatever its formula may have been. He describes the salt as losing $1\frac{1}{2}$ molecules of water at 100° , and the remainder at 135° . It has already been pointed out that determinations of the water in this salt are quite unreliable on account of the tendency to decomposition and the difficulty with which the water is driven off at about 110° . The figures given by Hautz are as follows:

	For salt undried.		For salt dried at 100° .	
	Calculated.	Found.	Calculated.	Found.
NH ₄	8.32	8.2	9.84	...
Mn	25.90	...	29.54	28.69
Cl	49.12	...	55.76	55.52
H ₂ O	16.66	17.4	4.86	4.09
	100.00		100.00	

These figures would be somewhat different if calculated on the basis of the atomic weights now in use; but even then the lack of agreement between the numbers calculated and those found by analysis would be too great, in some cases, to be attributed to errors of experiment. From these partial analyses Hautz derives the formula (using our present atomic weights) $\text{NH}_4\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ for the undried salt, and $\text{NH}_4\text{MnCl}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ for the salt dried at 100° .

It was not found possible to prepare this substance. Even

when a large excess of manganous chloride was present the salt $(\text{NH}_4)_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ was invariably obtained. From a consideration of all the evidence, the conclusion is drawn that the salt obtained by Hautz was really $(\text{NH}_4)_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ in an impure condition, and that no salt exists having the formula $\text{NH}_4\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$. This conclusion was quite unexpected, as it was naturally supposed that there would be an ammonium salt corresponding to the potassium salt obtained. The relations between all the members of this series of salts will be referred to farther on.

The salt $(\text{NH}_4)_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$, as obtained and analysed by v. Hauer, seems to have been quite impure. He describes it as crystallising in cubes of a yellow or pale red color, which became almost white after recrystallisation. This description is entirely erroneous, except in regard to the pale redness of the salt.

The belief in the existence of the salt $(\text{NH}_4)_2\text{MnCl}_4 \cdot \text{H}_2\text{O}$ rests on the authority of Rammelsberg and of Pickering. The former states that it crystallises in the regular system, and publishes a partial analysis in proof of the formula given by him. His figures are as follows:

	Calculated.	Found.
Mn	21.97	21.03
4Cl	56.52	...
2NH ₄	14.34	14.08
• H ₂ O	7.17	...
	100.00	

While the figures obtained in the case of ammonium are fairly close to those calculated, it should be observed that in the case of manganese the figures found are about $\frac{1}{10}$ of a unit nearer to the formula with *two* molecules of water of crystallisation, than to that given by Rammelsberg. Pickering obtained a salt crystallising in hard brown cubes, which after recrystallisation from water gave figures, on analysis, which "corresponded perfectly to the formula" $(\text{NH}_4)_2\text{MnCl}_4 \cdot \text{H}_2\text{O}$. Unfortunately these figures were not published.

In regard to this salt a series of experiments was carried out, the results of which are here given. The samples analysed were obtained under widely differing conditions.

I. Obtained by rapid cooling of a solution containing manganous chloride and ammonium chloride in proper proportions for the formula $(\text{NH}_4)_2\text{MnCl}_4$.

0.6610 gram gave 0.0985 gram Mn_2O_4 (10.73 per cent. Mn).

0.2733 gram gave 0.6521 gram AgCl (59.00 per cent. Cl).

II. Obtained by spontaneous evaporation of a solution of the mixed chlorides.

0.3703 gram gave 0.0771 gram Mn_2O_4 (15.00 per cent. Mn).

0.3401 gram gave 0.7668 gram AgCl (55.75 per cent. Cl).

III. A solution was evaporated by heat, and crystallisation allowed to take place by slow cooling.

0.5497 gram gave 0.1161 gram Mn_2O_4 (15.21 per cent. Mn).

0.2974 gram gave 0.6666 gram AgCl (55.43 per cent. Cl).

IV. Prepared by the same method.

0.3355 gram gave 0.0892 gram Mn_2O_4 (19.15 per cent. Mn).

0.2298 gram gave 0.4964 gram AgCl (53.42 per cent. Cl).

V. Obtained by the spontaneous evaporation of a solution containing a large excess of manganous chloride.

0.3557 gram gave 0.1008 gram Mn_2O_4 (20.41 per cent. Mn).

0.3693 gram gave 0.7870 gram AgCl (52.70 per cent. Cl).

VI. and VII. These are analyses of the precipitate first mentioned by Godeffroy,¹ which is produced when a saturated solution of manganous chloride in concentrated hydrochloric acid is added to a similar solution of ammonium chloride. As this precipitate had not been previously analysed, it was hoped that it might prove to be a definite compound. It is, however, a mixture of varying composition. Of the two samples obtained, the color of the second was much more decidedly pink than that of the first. They were both dried on a porous plate, and then to constant weight over caustic potash.

VI. Precipitated by mixing solutions at ordinary temperatures.

0.3432 gram gave 0.1056 gram Mn_2O_4 (22.19 per cent. Mn).

0.3112 gram gave 0.6572 gram AgCl (52.22 per cent. Cl).

VII. Precipitated by mixing solutions previously cooled to about 0°.

0.3667 gram gave 0.1202 gram Mn_2O_4 (23.61 per cent. Mn).

0.3592 gram gave 0.7367 gram AgCl (50.72 per cent. Cl).

These results form a series in which the percentage of manganese increases and that of chlorine decreases, as here arranged :

¹ Ber. der d. chem. Ges. 8, 9.

	Mn.	Cl.
I.	10.73	59.00
II.	15.00	55.75
III.	15.21	55.43
IV.	19.15	53.42
V.	20.41	52.70
VI.	22.19	52.22
VII.	23.61	50.72

The calculated percentages for the formula $(\text{NH}_4)_2\text{MnCl}_4 \cdot \text{H}_2\text{O}$, using accurate atomic weights, are Mn 21.90 and Cl 56.53. It is evident that no such salt was obtained. Only one substance in the above list was a definite compound, namely the fifth, already described as the salt $(\text{NH}_4)_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$. Its crystalline form was definite. I, II and III formed indefinite masses of ill-defined crystals. VI and VII were amorphous precipitates. IV crystallised, at least in part, in perfectly definite octahedrons. As the analysis showed it to be a mixture, it appears highly probable that the octahedrons consisted of impure ammonium chloride, while the remainder of the deposit contained a large amount of the double salt with *two* molecules of water. This might account for the fact that both Rammelsberg and Pickering state that the salt obtained by them is regular in crystallisation. Pickering obtained cubes. It seems probable that in some of the other specimens recorded in the above list manganous chloride was present as a mechanical admixture. As no definite directions are given for the preparation of the salt described by Rammelsberg and by Pickering, absolute proof of its non-existence can hardly be expected. The investigation above related seems, however, to give sufficient proof. It is to be remembered that the only published analytical evidence which is really in favor of the existence of the salt consists of one determination of the ammonium.

From the results obtained in this work with ammonium chloride, the conclusion is drawn that only one compound of that substance with manganous chloride has ever been found, namely the salt $(\text{NH}_4)_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$.

Experiments with Rubidium Chloride.

According to R. Godeffroy,¹ rubidium chloride forms with manganous chloride two compounds, differing, however, only in

¹ Archiv der Pharmacie [3] 12, 47; Zeitschr. des allg. österreichischen Apotheker-Vereines, 1875, 21.

the amount of water of crystallisation contained in them. One is described as a pale rose-red, crystalline powder, having the composition represented by the formula Rb_3MnCl_4 . By recrystallising this precipitate, crystals of the formula $\text{Rb}_3\text{MnCl}_4 \cdot 3\text{H}_2\text{O}$ are said to be obtained. The precipitate was here investigated first. It is obtained by bringing together concentrated solutions of manganese chloride and of rubidium chloride, concentrated hydrochloric acid having been used as the solvent in both cases. The precipitate was prepared several times under slightly different conditions of temperature. In every case it was dried according to the method already described under the experiments with ammonium chloride. On subsequent heating to about 105° in an air-bath, every specimen was found to give up water of crystallisation. Partial analyses of three of the samples are here recorded:

I. 2.6691 grams lost at 105° – 110° 0.2395 gram H_2O = 8.97 per cent. H_2O .

II. 0.5120 gram lost at 105° – 110° 0.0537 gram H_2O = 10.49 per cent. H_2O .

III. 1.3399 grams lost at 105° – 110° 0.1705 gram H_2O = 12.72 per cent. H_2O .

The precipitates thus dried were found to contain varying amounts of chlorine.

I. 0.3464 gram gave 0.5408 gram AgCl (38.61 per cent. Cl).

II. 0.3124 gram gave 0.5066 gram AgCl (40.10 per cent. Cl).

III. 0.3216 gram gave 0.5591 gram AgCl (42.99 per cent. Cl).

If these percentages of chlorine be calculated back so as to represent percentages in the salt *before* the combined water was driven off, they become—

I. 35.15 per cent. Cl .

II. 35.89 per cent. Cl .

III. 37.52 per cent. Cl .

All the precipitates were very pale pink in color, the tint being, however, noticeably darker in the case of the third than in the others.

The figures obtained by Godeffroy are as follows:

	Calculated for Rb_3MnCl_4 .	Found.
4Cl	38.71	38.48
Mn	14.95	14.00
2Rb	46.34	45.97
	100.00	98.45

From a consideration of all the above facts the conclusion is drawn that the precipitate produced by mixing concentrated solutions of manganous chloride and rubidium chloride in concentrated hydrochloric acid is not anhydrous and is not a single, definite chemical compound, but a mechanical mixture of variable composition. These conclusions harmonize with those arrived at in studying the similar precipitate produced in the case of ammonium chloride.

When the precipitate is dissolved in water and the solution evaporated, extremely pale, pink crystals are obtained, usually forming radiating groups. This substance Godeffroy found to have the composition represented by the formula $\text{Rb}_2\text{MnCl}_4 \cdot 3\text{H}_2\text{O}$, the salt losing two molecules of water at 100° and the remainder at 150° . After working on this salt for some time it was found that it encloses a considerable amount of water mechanically, which is only given off with extreme slowness in a desiccator, unless the salt has been previously thoroughly powdered. Godeffroy does not mention having taken this precaution, and it therefore seems probable that it was partly owing to the error introduced at this point that his analysis led to the formula with three molecules of water instead of the correct one with only two. At 150° the manganous chloride would become partly oxidised, and thus an additional loss in weight—and an additional error—would be obtained. Godeffroy's figures are here given:

	Calculated for $\text{Rb}_2\text{MnCl}_4 \cdot 3\text{H}_2\text{O}$.	Found.
2Rb	40.53	...
Mn	13.03	13.17
4Cl	33.65	33.83
2H ₂ O	8.76	8.54
H ₂ O	4.03	3.54
	100.00	

In the present investigation the following figures were obtained, the salt having been dried to constant weight, in powdered condition, over calcium chloride:

0.3589 gram gave 0.5099 gram AgCl (35.13 per cent. Cl), and 0.0677 gram Mn_2O_3 (13.59 per cent. Mn).

0.2856 gram lost at 105° – 110° 0.0259 gram H_2O = 9.07 per cent. H_2O , and gave 0.1707 gram RbCl (42.24 per cent. Rb).

	Calculated for $\text{Rb}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$.		Found.
2Rb	170.4	42.33	42.24
Mn	54.8	13.61	13.59
4Cl	141.48	35.14	35.13
2H ₂ O	35.92	8.92	9.07
	402.60	100.00	100.03

The composition of the salt, therefore, corresponds to that required by the formula $\text{Rb}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$. It is easily soluble in water and can be recrystallised. It readily loses all its water of crystallisation at 110° . It does not deliquesce in the air, and does not lose its water of crystallisation when placed over calcium chloride. This latter point needs, perhaps, further discussion in consideration of the method used for drying the salt for analysis. In the first place it is to be noted that the salt can be dried in ordinary dry air, provided it is in a finely powdered condition, though the process is more rapid over calcium chloride. That the water given off in this drying is not water of crystallisation is clear from three considerations: 1st. it varies in amount; 2d. on examining a crystal of the salt under a microscope, inclusions of water can be seen; 3d. a crystal does not lose its form or transparency when dried over calcium chloride.

Efforts to obtain a salt corresponding to $\text{KMnCl}_4 \cdot 2\text{H}_2\text{O}$ were made, but no such rubidium salt was found even when a considerable excess of manganous chloride was present. This investigation shows that, in all probability, the only definite compound of manganous chloride with rubidium chloride which is capable of isolation is the salt $\text{Rb}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$.

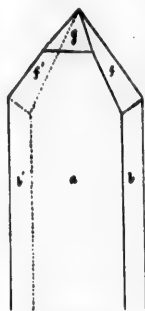


FIG. 5.

Crystallography of the salt.—It is obtained best by spontaneous evaporation of the aqueous solution. The crystals frequently form radiating groups. When well developed they form elongated tabular crystals. In habit they are not always the same, though a common type is that represented in Fig. 5. This consists of two individuals twinned and united along a plane running parallel to the long axis of the crystal. The crystallisation is triclinic, as shown by the optical properties and measurements of the angles. There is no reëntrant angle formed where the two parts of the twin unite, hence the composi-

tion face is not a crystallographic plane. The substance shows gliding phenomena. Its crystallography was not worked out in full. The measurements made are, however, pretty accurate, and it is believed that they, together with the rough drawing, will be sufficient for the satisfactory identification of the salt at any time. The cleavage is well marked parallel to the plane b .

The following values were obtained by measurement :

$$a : b = 84^{\circ} 57'.$$

$$a : b' = 95^{\circ} 5'.$$

$$a : f = 104^{\circ} 41'.$$

$$a : f' = 75^{\circ} 16'.$$

$$f : f' \text{ (over summit)} = 70^{\circ} 36\frac{1}{2}'.$$

$$a : g = 169^{\circ} 27'.$$

$b : f = b' : f' = 138^{\circ} 40\frac{1}{2}'$ or $141^{\circ} 42'$. The presence of vicinal planes made the true value of this angle uncertain. The plane g does not occur on the other side of the crystal at the same end. Good doubly-terminated crystals were not obtained.

Experiments with Cæsium Chloride.

In the papers already referred to Godeffroy claims to have found three distinct compounds of manganous chloride with cæsium chloride, namely, a precipitate Cs_2MnCl_4 and two crystalline salts $\text{Cs}_2\text{MnCl}_4 \cdot 3\text{H}_2\text{O}$ and $2(\text{Cs}_2\text{MnCl}_4) \cdot 5\text{H}_2\text{O}$. The precipitate is obtained under the same conditions as were mentioned in the case of ammonium chloride. The substance was prepared three times in slightly different ways, and a partial analysis was made in each case. On drying the precipitate, as in the previous experiments, over caustic potash, a constant weight was not obtained even after a period of two weeks. It is evident that this loss was due to the slow abstraction of water of crystallisation. The determinations of the combined water are necessarily approximate only. The salt was dried first on a porous plate, and then for a few hours over caustic potash before the determination was made.

I. Solutions slightly warmed at the time of precipitation :

0.6935 gram lost at 105° – 110° 0.0804 gram $\text{H}_2\text{O} = 11.59$ per cent. H_2O .

After thus drying, 0.3116 gram gave 0.0805 gram Mn_2O_3 (18.61 per cent. Mn), and 0.3001 gram gave 0.4375 gram AgCl (36.05 per cent. Cl).

II. Solutions cooled to about 0° at the time of precipitation:
 0.8523 gram lost at 105° – 110° 0.0922 gram H_2O = 10.82 per cent. H_2O .

After thus drying, 0.3242 gram gave 0.0843 gram Mn_2O_4 (18.73 per cent. Mn), and 0.3416 gram gave 0.4991 gram $AgCl$ (36.13 per cent. Cl).

III. The solution of manganous chloride was quite dilute, the acid in which it was dissolved being, as before, concentrated.

1.1491 grams lost at 105° – 110° 0.1189 gram H_2O = 10.35 per cent. H_2O .

After thus drying, 0.3589 gram gave 0.0925 gram Mn_2O_4 (18.56 per cent. Mn), and 0.3032 gram gave 0.4432 gram $AgCl$ (36.15 per cent. Cl).

	Calculated for $CsMnCl_2 \cdot 2H_2O$.	Found.		Calculated for $CsMnCl_2$.	Found.
$2H_2O$	10.90	11.59	Mn	18.66	18.61
		10.82			18.73
		10.35			18.56
			3Cl	36.14	36.05
					36.13
					36.15

The precipitate consists therefore of the salt $CsMnCl_2 \cdot 2H_2O$ in almost pure condition. After drying in an air-bath at 105° its composition corresponds to the formula $CsMnCl_2$. No compound of caesium chloride with manganous chloride in these proportions has hitherto been described. The results which Godeffroy obtained by analysis of the precipitate, prepared in the same way as the above, are:

	Calculated for Cs_2MnCl_4 .	Found.
2Cs	57.47	57.76
Mn	11.87	11.11
4Cl	30.66	31.04
	100.00	99.91

He seems to have analysed the salt only once. He does not state the manner in which the precipitate was dried. No explanation is here offered to account for the disagreement between these results and those obtained in the present investigation, but the author feels compelled to conclude that there was some serious error in the work of Godeffroy.

The pale pink precipitate just described is easily soluble in water. When the solution is evaporated, crystals are obtained belonging to the orthorhombic system. These can be recrystallised and are then found to be in pure condition. The salt is pale pink in color. It is not deliquescent in the air under ordinary conditions; but, when powdered, it loses its water of crystallisation in a good desiccator over calcium chloride. This loss, which is very slow, has already been referred to in the case of the impure, precipitated salt. It gives up its water of crystallisation very readily at 105° . For analysis the salt was dried by pressure between layers of filtering paper.

0.5028 gram lost at 105° 0.0548 gram $H_2O = 10.90$ per cent. H_2O .

The dried salt was then analysed.

0.4212 gram gave 0.1092 gram Mn_2O_4 (18.67 per cent. Mn), and 0.2416 gram $CsCl$ (45.29 per cent. Cs).

0.4480 gram gave 0.6547 gram $AgCl$ (36.14 per cent. Cl).

	Calculated for $CsMnCl_2 \cdot 2H_2O$.		Found.
$2H_2O$	10.90		10.90
	Calculated for $CsMnCl_2$.		Found.
Cs	132.7	45.20	45.29
Mn	54.8	18.66	18.67
3Cl	106.11	36.14	36.14
	293.61	100.00	100.10

The crystallised salt has therefore the formula $CsMnCl_2 \cdot 2H_2O$, and loses all of its water at 105° .

Crystallography of the salt.—The substance forms tabular crystals, which are shown by their optical properties and angular measurements to be orthorhombic (Fig. 6). The forms observed were, oP , $\infty P\infty$, $\infty P\infty$, ∞P and $P\bar{2}$. The reflections obtained in the goniometer were not, as a rule, very good, and the exact values of the angles are rendered additionally doubtful in some cases, owing to the presence of vicinal planes.

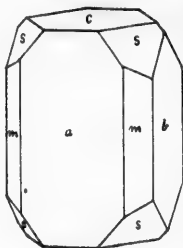


FIG. 6.

$c = oP$, $[001]$.

$a = \infty P\infty$, $[100]$.

$b = \infty P\infty$, $[010]$.

$m = \infty P$, $[110]$.

$s = P\bar{2}$, $[122]$.

By comparing together many measurements the following values were obtained, which appeared sufficiently trustworthy for the determination of the axial ratios:

$$s:a = 116^{\circ} 14'.$$

$$s:c = 124^{\circ} 7'.$$

$$s:s = 127^{\circ} 32'.$$

$$m:b = 128^{\circ} 6'.$$

$$m:a = 141^{\circ} 54'.$$

The axial ratios deduced are, $\tilde{a} = .7919$, $\tilde{b} = 1$, $\tilde{c} = 1.2482$.

When the angles given above are calculated from these axial ratios they become:

$$s:a = 116^{\circ} 14'.$$

$$s:c = 124^{\circ} 7'.$$

$$s:s = 127^{\circ} 32'.$$

$$m:b = 128^{\circ} 22\frac{1}{2}'.$$

$$m:a = 141^{\circ} 37\frac{1}{2}'.$$

The cleavage is parallel to a .

If caesium chloride be added to a solution of the salt $\text{CsMnCl}_4 \cdot 2\text{H}_2\text{O}$, crystals are deposited, on evaporation, which are quite different in habit from those previously obtained, and are much paler in color. These proved to be the salt corresponding to that obtained when working with rubidium chloride, having the formula $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$. This is probably the compound obtained by Godeffroy and regarded by him as two different salts, namely $\text{Cs}_2\text{MnCl}_4 \cdot 3\text{H}_2\text{O}$ when crystallised out of an aqueous solution, and $2(\text{Cs}_2\text{MnCl}_4) \cdot 5\text{H}_2\text{O}$ when crystallised out of a solution in concentrated hydrochloric acid. The salt is not deliquescent in ordinary air, and retains its water of crystallisation when dried in an ordinary desiccator. For analysis it was dried, in the form of a fine powder, over calcium chloride. Its water of crystallisation is readily driven off at 105° .

0.4311 gram gave 0.0663 gram Mn_2O_3 (11.08 per cent. Mn), and 0.2923 gram CsCl (53.53 per cent. Cs).

0.2204 gram lost at 105° 0.0162 gram $\text{H}_2\text{O} = 7.35$ per cent. H_2O , and gave 0.2532 gram AgCl (28.41 per cent. Cl).

	Calculated for $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$.		Found.
2Cs	265.4	53.34	53.53
Mn	54.8	11.01	11.08
4Cl	141.48	28.43	28.41
2H ₂ O	35.92	7.22	7.35
	497.60	100.00	100.37

The salt corresponds in composition to the formula $\text{Cs}_3\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$. Godeffroy's analyses of this salt, which seemed to indicate the presence of three molecules of water, were no doubt vitiated by the incomplete drying of the salt before analysis, as was pointed out in the case of the corresponding rubidium compound. His figures are:

	Calculated for $\text{Cs}_3\text{MnCl}_4 \cdot 3\text{H}_2\text{O}$.	Found.
2Cs	51.39	...
Mn	10.65	10.07
4Cl	27.50	27.24
3H ₂ O	10.46	10.96 and 10.23
	100.00	

No evidence was found in favor of the existence of a salt of this composition.

Crystallography of the salt $\text{Cs}_3\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$.—This was not worked out in full, but the following details are given to serve for the identification of the substance. It is triclinic in crystallisation, resembling, in general appearance, the corresponding rubidium salt. The cleavage is, however, parallel to the best developed face, a , which is not true of the rubidium compound. Another difference between the two salts is observed in regard to the method of twinning. The caesium salt shows a reëntrant angle of about 169° where the two individuals are joined, while the rubidium salt does not. Other differences are evident from the measurements.

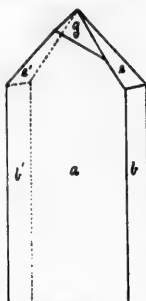


FIG. 7.

Fig. 7 gives a rough drawing of a crystal of this salt, not twinned. Most of the measurements here given are the mean of two, made on different crystals. They generally agreed within a few minutes. The last two are only approximate. The plane g occurs only on one side of the crystal at each end.

The following measurements were obtained:

- $a:b = 95^\circ 27'$ (hence $a:b' = 84^\circ 33'$).
- $a:g = 139^\circ 24'$.
- $b:e = 151^\circ 6'$.
- $b':e' = 154^\circ 1\frac{1}{2}'$.
- $e:e'$ (over summit) $= 54^\circ 53\frac{1}{2}'$.
- $a:e = 85\frac{1}{2}^\circ$.
- $a:e' = 97\frac{1}{2}^\circ$.

A careful attempt was made to prepare the salt $2(\text{Cs}_2\text{MnCl}_4) \cdot 5\text{H}_2\text{O}$ by following the directions of Godeffroy as closely as possible. The solution in concentrated hydrochloric acid, which remained over the precipitate of slightly impure $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$, was evaporated without the aid of heat, by drawing a stream of dry air over it for several months. A few small crystals were at length obtained. These were very pale pink in color and seemed to be the salt $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$. On attempting to isolate the compound, after further evaporation of the solution, it was found that some other substance, probably manganous chloride, had crystallised out as well. As it was evidently impossible to obtain a pure product without recrystallisation, which would have been to depart from the conditions mentioned by Godeffroy, the subject was not followed up. In view of the existence of the salt $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$ and of the non-existence of the salt $\text{Cs}_2\text{MnCl}_4 \cdot 3\text{H}_2\text{O}$ described by Godeffroy, and in view of the weak evidence brought forward to prove the existence of the salt $2(\text{Cs}_2\text{MnCl}_4) \cdot 5\text{H}_2\text{O}$, the matter did not seem worthy of further investigation. The existence of the salt under consideration seems in the highest degree improbable.

Experiments with Magnesium Chloride and with Magnesium Bromide.

In this part of the work it was found more satisfactory to use alcohol and water, instead of water alone, as a solvent. Seventy per cent. of alcohol is probably about the best strength. The solutions were always kept acidified to prevent the decomposition of the magnesium salt. When a solution of manganous chloride and magnesium chloride is evaporated the two chlorides unite, forming one or, perhaps, more compounds, the appearance of which varies greatly according to the exact conditions of formation. Many experiments were performed. In general a compound was obtained crystallising in flattened, sometimes feather-like crystals, which were never found to be pure. On one occasion these plates were left standing for several weeks in contact with the mother-liquor, and were found to be entirely transformed into crystals almost round in shape, usually about $\frac{1}{4}$ cm. in diameter. They could not be investigated crystallographically, owing to their rapid deliquescence. Though not obtained in pure condition, analysis shows that this salt corresponds in composition to the bromide, described below, which is much more easily worked

with. The flattened crystals of the chloride seem to have the same composition as the rounded ones, though they were never obtained in a condition approaching purity. As this double chloride, in whatever form it is obtained, is deliquescent in the air and loses some of its water of crystallisation over calcium chloride, a satisfactory analysis of it could not be made. It was dried for a few hours in a desiccator, but was found when analysed to contain, still, a considerable amount of hygroscopic water. For the method of analysis see below.

0.7608 gram gave 0.1981 gram Mn_2O_3 (18.76 per cent. Mn), and 0.1569 gram $\text{Mg}_3\text{P}_2\text{O}_7$ (4.50 per cent. Mg).

0.9970 gram gave 1.4961 grams AgCl (37.11 per cent. Cl).

The water of crystallisation is not all given off without decomposition of the salt.

	Calculated for $\text{Mn}_2\text{MgCl}_6 \cdot 12\text{H}_2\text{O}$.		Found.
2Mn	109.6	19.52	18.76
Mg	24.21	4.31	4.50
6Cl	212.22	37.79	37.11
12H ₂ O	215.52	38.38	...
	561.55	100.00	

If we allow for the hygroscopic water, which seems to be present, 1½ per cent., we obtain Mn 19.15, Mg 4.59 and Cl 37.88 per cent. The salt, though somewhat impure, evidently corresponds in composition to the bromide mentioned below, and has the formula $\text{Mn}_2\text{MgCl}_6 \cdot 12\text{H}_2\text{O}$.

As noticed near the commencement of this paper, when a large excess of manganous chloride is present the salt $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ is produced. No evidence was found of the existence of a salt containing manganous chloride and magnesium chloride in the proportions of one molecule to one.

When manganous bromide and magnesium bromide are present in a solution in the proportion of two molecules of the former to one of the latter, and the solution is evaporated, a double salt crystallises out on cooling. The substance usually forms a compact mass of red crystals at the bottom of the beaker. It can be recrystallised, but well-formed, individual crystals are seldom obtained. It is deliquescent in the air. No loss of water of crystallisation was observed when it was dried over calcium chloride. The most convenient method found for the separation

of the metals, in analysis, was as follows: Decompose the salt with a small amount of sulphuric acid, and heat till all the hydrochloric (or hydrobromic) acid is driven off; then add a solution of ammonium chloride, and heat nearly to boiling. Add gradually ammonium sulphide free from carbonate. Keep hot for about an hour, and then filter and wash. The manganous sulphide is then dissolved in dilute hydrochloric acid, filtered free from sulphur, and precipitated as carbonate after driving off the hydrogen sulphide. The solution containing the magnesium is evaporated, acidified, filtered from sulphur, and the magnesium then precipitated in the usual way.

The water of crystallisation present in this salt cannot be determined directly on account of the decomposition of the substance. That decomposition actually takes place before all the water is given off is evident from the darkening in color, and the fact that part of the salt is rendered insoluble in water. The substance was obtained in almost pure condition without recrystallisation, as shown by the following figures obtained:

0.6679 gram gave 0.1235 gram Mn_2O_3 (13.32 per cent. Mn), and 0.0915 gram $Mg_2P_2O_7$ (2.99 per cent. Mg).

0.6654 gram gave 0.8998 gram AgBr (57.55 per cent. Br).

After heating the salt for several hours not far above 100° , and then for seven hours at about 150° , the loss in weight represented 16.27 per cent. of water. Considerable decomposition had taken place.

	Calculated for $Mn_3MgBr_6 \cdot 12H_2O$.		Found.
2Mn	109.6	13.24	13.32
Mg	24.21	2.93	2.99
6Br	478.56	57.80	57.55
12H ₂ O	215.52	26.03	...
	827.89	100.00	

The formula of the salt is therefore $Mn_3MgBr_6 \cdot 12H_2O$, corresponding to that of the impure chloride obtained.

Negative Results.

No compound of lithium chloride with manganous chloride was found, but it is worthy of note that the aqueous solution of the mixed chlorides has, when concentrated, a *green* color, which becomes quite brilliant when the solution is heated. When potas-

sium chloride is present instead of lithium chloride, the hot solution appears greenish-brown.

Some evidence of the formation of a compound of sodium chloride with manganous chloride was obtained, but it was not found possible to isolate the product in sufficiently pure condition for analysis, owing to the very great excess of manganous chloride present.

Unsuccessful attempts were made to obtain compounds of manganous chloride with the chlorides of copper (cuprous and cupric), calcium, strontium and barium. A concentrated solution of the mixed chlorides of calcium and manganese possesses a green color, somewhat like that observed in the case of lithium chloride. An almost amorphous mass was obtained, containing manganous chloride and calcium chloride, which may have been an impure double salt, but it was not in a fit condition for analysis.

Conclusion.

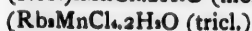
The work was not continued beyond magnesium. Compounds have, however, been described of manganous chloride with cadmium chloride¹ and with mercuric chloride.² We find, then, that manganous chloride combines with the chlorides of potassium, rubidium and caesium; but that, following the families according to the periodic system, there is, after caesium, a gap of considerable length, including chiefly the chlorides of calcium, strontium and barium. Manganous chloride appears incapable of combining with any of the chlorides between caesium and magnesium. The latter, however, marks the commencement of a new series, with every member of which manganous chloride can probably combine. The explanation of these facts is simple if we assume that the acidic and basic powers of manganous chloride are about equal to those of strontium chloride, and that in its compounds with the chlorides of potassium, rubidium and caesium, manganous chloride acts in its acidic capacity, while in its compounds with the chlorides of magnesium (zinc?), cadmium, etc., it acts in its basic capacity. Taking this view we should expect a break to occur between these two series.

The compounds hitherto described are given in tabular form at the commencement of the paper. A comparison between that list and the one given below, of the compounds actually found to

¹ v. Hauer, Jour. für pr. Chem. 68, 393.

² v. Bonsdorff, Pogg. Ann. 17, 247.

exist, will show that the regularity in the series is much greater than was to be supposed.



It will be noticed that these salts are very irregular from a crystallographic standpoint. It is strange that two gaps should occur in the left-hand series. Special efforts were made to obtain both of the missing compounds, but without success. Perhaps the entire dissimilarity in crystal system and habit between the potassium and the caesium salt may be taken as evidence that, though chemically analogous, the two compounds are not really very closely related to each other.

PART II.

ANTIMONY COMPOUNDS.

Since two double chlorides containing antimony had been described by Godeffroy as containing six molecules of alkali chloride to one of antimony chloride, and were therefore to be regarded as exceptions to the general rule governing the composition of the double halides, it was thought best to repeat the work of Godeffroy. The exceptional salts referred to are



Experiments with Caesium Chloride.

It is necessary, first of all, to give a brief review of the work of Godeffroy on this subject. In 1874¹ he published the first statements in regard to the precipitate obtained by mixing solutions of antimony chloride and caesium chloride in concentrated hydrochloric acid. This precipitate was recrystallised several times and analysed. The mean of five analyses gave him the following results:² Chlorine, 33.419 per cent.; antimony, 30.531 per cent. From these figures he derives the formula $\text{SbCl}_4 \cdot \text{CsCl}$. The

¹ Zeitschr. des allg. österr. Apotheker-Vereines, 1874, 161.

² Ber. der d. chem. Ges. 7, 375.

numbers calculated from the formula are: Chlorine, 35.93 per cent.; antimony, 30.37 per cent. Godeffroy regarded the precipitate and the crystalline salt as identical in composition, but gives no definite proof in support of this idea. In the year following¹ he published a complete analysis of the salt, assigning to it an entirely new formula, namely, $\text{SbCl}_3 \cdot 6\text{CsCl}$. The results he gives are as follows:

	Calculated for $\text{SbCl}_3 \cdot 6\text{CsCl}$.	Found.
9Cl	25.77	25.68
Sb	9.83	9.40
6Cs	64.40	63.98
	100.00	99.06

While the figures found agree fairly well with those calculated, the fact must not be lost sight of that there is a discrepancy between the figures found in 1874 and those found in 1875 of over seven units in the case of chlorine and of over twenty-one units in the case of antimony. As no explanation of this difference is given, it seems necessary to attribute it to experimental errors in analysis. The methods used in the later investigation are worthy of notice in this connection. The salt was dissolved in water acidified with tartaric acid, and after precipitation of the chlorine as silver chloride, the antimony was precipitated as sulphide. The sulphide was then oxidised with nitric acid, and the sulphuric acid thus obtained was estimated in the usual way. The amount of antimony was then calculated from the amount of barium sulphate obtained.

In the present investigation the precipitate was prepared in the manner described, the conditions of temperature being, however, slightly varied in the different experiments. The antimony chloride used for the first was purified by precipitation as oxychloride, that for the second by distillation. The precipitate of the double salt is very pale yellow in color. This does not appear to be due to impurities. The crystallised salt has the same color. The precipitates were dried for analysis in the manner before described. The methods of analysis will be referred to later on in the paper.

I. 0.6051 gram gave 0.2146 gram Sb_2S_3 (25.32 per cent. Sb), and 0.3162 gram CsCl (41.26 per cent. Cs).

II. 0.7470 gram gave 0.2682 gram Sb_2S_3 (25.63 per cent. Sb), and 0.3880 gram CsCl (41.01 per cent. Cs).

¹ Zeitschr. des allg. österr. Apotheker-Vereines, 1875, 21.

A third preparation of the precipitate, using the same redistilled antimony chloride as was used for the second, gave 25.38 per cent. of antimony. The composition of the precipitate appears therefore to be nearly constant. The figures obtained correspond pretty closely to those required for a salt of the formula $2\text{SbCl}_5 \cdot 3\text{CsCl}$.

	Calculated for $\text{Cs}_3\text{Sb}_2\text{Cl}_9$.	Found.	
Sb	25.03	25.32	25.63
Cs	41.66	41.26	41.01

This precipitate is soluble in hot dilute hydrochloric acid, though only slightly soluble in the cold. On evaporation, crystals of various habits are obtained according to the conditions. They generally appear as needles or thin prisms when deposited by the cooling of a hot solution; while by spontaneous evaporation they form thicker prisms or irregular plates, having a rough pseudo-hexagonal appearance produced by twinning. Two or three different samples of the crystallised salt were analysed. The composition of all of them agreed with the formula proposed.

0.3112 gram gave 0.1641 gram CsCl (41.63 per cent. Cs).

0.1940 gram gave 0.0684 gram Sb_2S_3 (25.16 per cent. Sb).

0.2059 gram gave 0.2770 gram AgCl (33.27 per cent. Cl).

0.4237 gram gave 0.1499 gram Sb_2S_3 (25.25 per cent. Sb), and 0.2240 gram CsCl (41.74 per cent. Cs).

0.2203 gram gave 0.2938 gram AgCl (32.97 per cent. Cl).

	Calculated for $\text{Cs}_3\text{Sb}_2\text{Cl}_9$.		Found.	
3Cs	398.1	41.66	41.63	41.74
2Sb	239.2	25.03	25.16	25.25
9Cl	318.33	33.31	33.27	32.97
	955.63	100.00	100.06	

As this salt was obtained with the greatest ease and according to the method described by Godeffroy, the author feels justified in drawing the conclusion that this is the compound for which Godeffroy proposed the formula $\text{SbCl}_5 \cdot \text{CsCl}$ and, later, $\text{SbCl}_5 \cdot 6\text{CsCl}$, the correct formula being $\text{Cs}_3\text{Sb}_2\text{Cl}_9$. This salt is therefore no longer to be considered as an exception to the general rule regarding the composition of the double halides. This is the only compound of caesium chloride and antimony chloride which is easily obtained. It may be that a salt of the formula CsSbCl_6 could be produced under suitable conditions, but the salt above

described was the only one identified in the present investigation, though efforts were made to obtain others.

The crystallography of this salt was not worked out. A few details were, however, obtained. It usually crystallises in elongated prisms. These belong to the orthorhombic system, but are sometimes twinned, when very short, in such a way as to give a rough pseudo-hexagonal form. Such a twin is represented in Fig. 8. The three individuals combined in the crystal can be distinguished by examination in parallel polarised light.

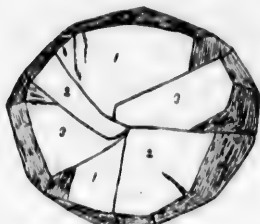


FIG. 8.

Experiments with Rubidium Chloride.

By evaporation of a dilute hydrochloric acid solution containing antimony chloride and rubidium chloride, Godeffroy¹ obtained tabular crystals of a double salt, to which he gave the formula $\text{SbCl}_3 \cdot 6\text{RbCl}$. This was analysed by the same method as that described under caesium chloride. The following are the figures given by Godeffroy:

	Calculated for $\text{SbCl}_3 \cdot 6\text{RbCl}$.	Found.
9Cl	33.47	33.45
Sb	12.79	13.10
6Rb	53.74	53.06
	100.00	99.61

A substance corresponding to Godeffroy's description was easily obtained by following his directions, and crystallised out of the solution in dilute hydrochloric acid in beautiful, colorless, six-sided plates, tables, or thicker crystals, according to the conditions. The salt has a very strong crystallising force. It is readily soluble in dilute hydrochloric acid, but less so in the concentrated acid.

By mixing concentrated solutions of rubidium chloride and of antimony chloride in concentrated hydrochloric acid, the double salt is formed as a distinctly crystalline precipitate. Repeated analyses show that the composition of this salt does not corres-

¹ *Zeitschr. des allg. österr. Apotheker-Vereines*, 1875, 21.

pond to the formula proposed by Godeffroy. The substance was prepared under varying conditions, being crystallised out either by slow cooling of the solution, or by sudden cooling, or by spontaneous evaporation. In the first experiment the two chlorides were mixed in the proportions required by the formula of Godeffroy. In the other cases no special care was taken in regard to the proportions. The composition of the salt formed did not vary appreciably. All the analyses made, in this part of the investigation, are here given, except one attempt to determine rubidium as nitrate, which was quite untrustworthy. The variations from the normal composition are no doubt due to experimental errors, or to the presence of slight impurities in some specimens of the salt.

I. 0.5720 gram gave 0.1902 gram Sb_2S_3 (23.73 per cent. Sb), and 0.8538 gram AgCl (36.91 per cent. Cl).

II. 0.4174 gram gave 0.1401 gram Sb_2S_3 (23.96 per cent. Sb), and 0.2297 gram RbCl (38.89 per cent. Rb).

0.3190 gram gave 0.4772 gram AgCl (36.99 per cent. Cl).

III. 0.4028 gram gave 0.1348 gram Sb_2S_3 (23.89 per cent. Sb), and 0.6007 gram AgCl (36.88 per cent. Cl).

0.6881 gram gave 0.3769 gram RbCl (38.71 per cent. Rb).

IV. 0.2728 gram gave 0.4071 gram AgCl (36.90 per cent. Cl).

V. 0.3359 gram gave 0.1125 gram Sb_2S_3 (23.90 per cent. Sb), and 0.1850 gram RbCl (38.92 per cent. Rb).

A tabular view of these results will make the matter clearer.

	Calculated ¹ for $\text{SbCl}_2 \cdot 6\text{RbCl}$.	Found by Godeffroy.	Found by the Author.			
			I.	II.	III.	IV and V.
Sb	12.60	13.10	23.73	23.96	23.89	23.90
6Rb	53.86	53.06	...	38.89	38.71	38.92
9Cl	33.54	33.45	36.91	36.99	36.88	36.90

These figures show that the salt obtained in the present investigation is a definite chemical compound, which does not correspond in composition to the numbers calculated from Godeffroy's formula. That this salt is really identical with that obtained by Godeffroy, in spite of the great difference between the analytical results in the two cases, is proved by several considerations. This salt is obtained with the greatest ease, much more readily than any other

¹ These figures differ slightly from those calculated by Godeffroy, owing to the use of different atomic weights in the two cases.

compound of rubidium chloride with antimony chloride. Of the three salts found this one contains the largest percentage of rubidium, and therefore approaches more nearly than either of the others to the composition required by Godeffroy's formula. The directions of Godeffroy were followed closely in preparing the salt, and in one case at least the two chlorides were present in solution in the proportions required by the above formula. The salt was examined crystallographically by Streng.¹ He describes it as forming hexagonal tables by a combination of the basal plane and fundamental pyramid, with a very slight development of the fundamental prism. In the present investigation no distinct development of the prism was observed. The pyramid faces were strongly striated in a horizontal direction, so that accurate measurements were impossible. The mean of three measurements of $P : P$ over a middle edge gave him $129^{\circ} 30'$, from which he calculated the axial ratio $a : c$ as $1 : 1.836$. The crystals obtained in the present investigation agree with the description of Streng. The angle measured by him was here found to vary between 127° and 131° , though the striations on the crystals prevented anything but the roughest measurements. Stauroscopic examination shows that the crystals are not really hexagonal in crystallisation; but as Streng does not seem to have examined his crystals optically, this disagreement in regard to the crystal system cannot be considered as evidence in favor of the two salts being different. The substance as prepared in this investigation was, to all outward appearance, hexagonal in crystallisation, and agreed exactly, except in the points mentioned, with the descriptions given by Godeffroy and by Streng. There can therefore be little doubt that the substances as obtained in the two investigations were identical. The conclusion is therefore drawn that no salt exists having the formula $SbCl_3 \cdot 6RbCl$.

As the five partial analyses already given showed that the formula of the salt was by no means simple, the matter was taken up again, with a view to obtaining a quantity of the salt in as pure a condition as possible, and then making several analyses. Having prepared a considerable amount of the substance, it was recrystallised five times from dilute hydrochloric acid. In the last two crystallisations the solution was cooled rapidly, so that the salt was deposited in very small, six-sided scales, possessing

¹ Archiv der Pharmacie [3] 9, 343.

a beautiful, pure white, lustrous appearance. The final drying of the compound was as follows: It was first of all dried by pressure between layers of filtering paper previously washed with hydrochloric acid, and was then finely powdered and placed on a watch-glass in a desiccator over phosphorus pentoxide. It was weighed from day to day until the loss in twenty-four hours was not perceptible, the weighings being made to the tenth of a milligram. In this way over two grams of the salt were obtained. The methods of analysis used are now to be described. In nearly all the analyses of salts containing antimony, the methods used were essentially the same as those here given.

The salt was dissolved in dilute hydrochloric acid in an Erlenmeyer flask and the solution heated to incipient boiling. Carefully washed hydrogen sulphide was then passed in until the solution was nearly cold. The flask was then tightly closed and left for at least an hour, when it was heated again to about 60° . The antimony sulphide was collected in a Gooch crucible, the filtration being performed while the liquid was hot. The precipitate was then washed with freshly prepared hydrogen sulphide water and afterward dried for about an hour at 105° . The crucible was then placed in a small air-bath filled with carbon dioxide, into which a current of the washed and dried gas was kept passing. The temperature of this bath was slowly raised to 200° and the flame then extinguished. The sulphide of antimony obtained in this way was black and anhydrous. It was found that all the water can be driven off from the sulphide without converting it into the black form, but the process is very slow. When the black sulphide was heated to 200° – 220° for a few hours a slight loss in weight was observed in almost all cases. This may have been due to the decomposition of a minute quantity of oxychloride of antimony present. One precipitation of the sulphide (the fourth) was made after adding a small quantity of tartaric acid to the solution. The precipitate formed in this case also suffered a very slight loss in weight on continued heating. If the presence of oxychloride of antimony be the cause of this reduction in weight it proves that, under the conditions mentioned, excess of hydrogen sulphide does not entirely decompose oxychloride of antimony, even when acting for so long a time as three hours on the precipitate, the solution being kept warm during one hour. The first weighing of the precipitate was the one assumed to be correct in every

case. The subsequent loss in weight was so slight (usually about one-tenth of a milligram in half an hour's heating at 210°), that no great error can have been introduced by neglecting it, whatever may have been its actual cause. The use of carbon dioxide to prevent the presence of oxygen in the solution during or after the precipitation of the antimony sulphide, seems to be quite unnecessary if the above directions be followed.

The rubidium was determined as chloride by evaporation of the filtrate, in which it was contained, in a platinum vessel. Before weighing, it was dried at about 230° and finally heated for a few moments to incipient redness. Special experiments showed that about one-tenth of a milligram of rubidium chloride was lost in the final heating. A correction was therefore made for that loss. The amount of solid matter obtained by the action of the hot solution on the glass during the precipitation of the antimony was determined by a blank experiment under the same conditions. A correction for this gain in weight was introduced in each determination of rubidium.

Chlorine was usually determined by precipitation as silver chloride in a solution of the salt in water acidified with tartaric and nitric acids. The silver chloride was afterwards dissolved in ammonia and reprecipitated. Determination of the chlorine after precipitation of the antimony as sulphide was found extremely difficult. The presence of an excess of free hydrochloric acid seems necessary to bring the antimony sulphide into a condition suitable for filtration.

As the determination of the atomic ratio between antimony and rubidium seemed to promise to give results containing the slightest errors, special stress was laid, in the following analyses, on that ratio. The analyses of the salt gave these results:

I. 0.3844 gram gave 0.1288 gram Sb_2S_3 (23.915 per cent. Sb), and 0.2129 gram RbCl (39.137 per cent. Rb).

II. 0.4401 gram gave 0.1476 gram Sb_2S_3 (23.937 per cent. Sb), and 0.2436 gram RbCl (39.113 per cent. Rb).

III. 0.3936 gram gave 0.1316 gram Sb_2S_3 (23.864 per cent. Sb), and 0.2175 gram RbCl (39.049 per cent. Rb).

IV. 0.3867 gram gave 0.1297 gram Sb_2S_3 (23.939 per cent. Sb).

V. 0.4078 gram gave 0.6115 gram AgCl (37.08 per cent. Cl).

The atomic ratios of antimony to rubidium as deduced from the three analyses are:

- I. Sb: Rb as 1 : 2.297.
 II. Sb: Rb as 1 : 2.294.
 III. Sb: Rb as 1 : 2.297.
 Mean Sb: Rb as 1 : 2.296.

From this the following ratios are derived. They are the only ones, at all simple, in which the figures are approximately whole numbers:

- Sb: Rb as 4 : 9.184
 Sb: Rb as 7 : 16.072
 Sb: Rb as 10 : 22.960

The simplest of these ratios, 4 to 9, must be rejected, as the experimental errors due to impurities in the salt or to defects in the analytical methods can hardly have been as great as those which would be indicated by the formula $4\text{SbCl}_3 \cdot 9\text{RbCl}$. The figures calculated from the ratios 7 to 16 and 10 to 23 are given below, together with the analytical results obtained by taking the mean of the determinations made with this last sample of the salt. That these results are uniformly higher than those found in the former analyses is probably due to imperfect drying of the salt in the earlier samples. The atomic weights used are Sb 119.6, Rb 85.2, Cl 35.37.

	Calculated for $7\text{SbCl}_3 \cdot 16\text{RbCl}$	Calculated for $10\text{SbCl}_3 \cdot 23\text{RbCl}$	Found.
Sb	23.86	23.776	23.91
Rb	38.85	38.957	39.10
Cl	37.29	37.267	37.08
	100.00	100.000	100.09

It will be seen that the agreement between the calculated composition and that found is closer for the larger formula than for the smaller. Assuming the larger formula to be correct, the disagreement between the figures may be due to errors in analysis, impurities present in the salt, and also perhaps to inaccuracy in the atomic weights used. While it is evidently impossible from these figures to establish the formula of this compound on a firm basis, the analyses prove that the salt is unusually complex in composition, and indicate that the most probable formula is $\text{Sb}_{10}\text{Rb}_{23}\text{Cl}_{52}$.

The salt is extremely stable in some respects. Though easily decomposed by water, as would be expected, it can be heated

in an air-bath to a very high temperature without undergoing any appreciable change. At 230° (several degrees above the boiling-point of antimony chloride) it was found to suffer slow decomposition, with loss of weight.

Stauroscopic examination of the salt shows that it is only *pseudo*-hexagonal, being in reality optically biaxial and positive. The acute bisectrix is almost (perhaps quite) normal to the basal plane. The optical behavior of the substance seems to indicate that it is usually composed of a series of superposed plates, with the planes of their optic axes not coincident. In some cases the crystals do not become dark in any position when rotated between crossed nicols. Thinner plates sometimes show an interference figure similar to that produced by two superposed plates of muscovite, with the planes of their optic axes at right angles. The thinnest plates show sharp extinction, and give an interference figure which

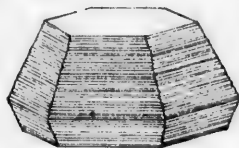


FIG. 9.

apparently denotes orthorhombic symmetry. Other plates show a sort of extinction wave or brush, which traverses the crystal when it is rotated between crossed nicols in parallel polarised light. Owing to the striations on the crystals (Fig. 9), no conclusions in regard to the system to which they

belonged could be drawn from the measurements of the angles. The cleavage of the salt is basal and well marked.

Mr. C. P. Brigham, working in this laboratory, has obtained a double salt of bismuth and rubidium chlorides, which, as he has shown, corresponds in formula to the salt above described.

On adding a considerable excess of antimony chloride to a solution of the complex salt discussed above, and evaporating, crystals of an entirely different form are obtained. These were not investigated crystallographically, but may be described as compact crystals, sometimes resembling a rhombohedron in general shape. The are pale yellow in color. This is noteworthy, because the more complex salt (described above) and the simpler one (discussed below) are both colorless. It is to be remembered, however, that the salt $\text{Cs}_2\text{Sb}_2\text{Cl}_6$ is also yellow. As the formula of this rubidium salt is not very simple, and as the substance could not be recrystallised, on account of the strong tendency towards the formation of the very complex salt, the formula suggested

below can hardly be considered as definitely established. The analytical results obtained from different samples varied considerably, and it does not appear possible to obtain the salt in pure condition.

One sample gave the following results:

0.3382 gram gave 0.1348 gram Sb_2S_3 (28.45 per cent. Sb), and 0.1560 gram RbCl (32.60 per cent. Rb).

0.2712 gram gave 0.4217 gram AgCl (38.45 per cent. Cl).

In another sample 0.1530 gram gave 0.2392 gram AgCl (38.66 per cent. Cl).

	Calculated for $3\text{SbCl}_2 \cdot 5\text{RbCl}$.		Found.
3Sb	358.8	28.03	28.45
5Rb	426.0	33.28	32.60
14Cl	495.18	38.69	38.45 and 38.66
	1279.98	100.00	99.50

In view of the fact that this salt is only formed in presence of an excess of antimony chloride, the above results may be considered as almost conclusive evidence in favor of the formula $\text{Rb}_5\text{Sb}_3\text{Cl}_{14}$. This salt is stable in comparatively dry air.

If the excess of antimony chloride added in the experiment last described be *very* great, a colorless salt crystallising in elongated, apparently orthorhombic, crystals is obtained, instead of the yellow salt. These crystals have brilliant faces when fresh, but on exposure to the air under ordinary conditions they soon become covered with an opaque white deposit, which probably consists of oxychloride of antimony, formed by surface decomposition of the salt. The compound was found to have a very simple formula, though the presence of so large an excess of antimony chloride at the time of its formation naturally makes the analytical results somewhat unsatisfactory. The salt cannot, of course, be recrystallised. As in the case of the salt just described, it was prepared for analysis merely by drying between filtering paper and then in a desiccator over calcium chloride.

0.4343 gram gave 0.2133 gram Sb_2S_3 (35.05 per cent. Sb), and 0.1489 gram RbCl (24.23 per cent. Rb).

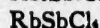
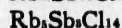
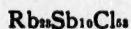
0.4563 gram gave 0.2242 gram Sb_2S_3 (35.07 per cent. Sb), and 0.7495 gram AgCl (40.62 per cent. Cl).

	Calculated for RbSbCl_4		Found.
Rb	85.2	24.60	24.23
St	119.6	34.54	35.05 and 35.07
4Cl	141.48	40.86	40.62
	346.28	100.00	99.90

The formula of this salt is therefore RbSbCl_4 .

Summary.

The following is a list of the compounds of antimony chloride, with the chlorides of rubidium and caesium obtained in this investigation. The formula of the first of the rubidium salts must be considered as somewhat doubtful.



These formulas show that the elements in question have a marked tendency towards the formation of complex double chlorides. The most important conclusion, however, to be drawn from the present investigation is that neither the salt described by Godeffroy as $\text{SbCl}_3 \cdot 6\text{CsCl}$ nor that described as $\text{SbCl}_3 \cdot 6\text{RbCl}$ corresponds in composition to the formula proposed by him.

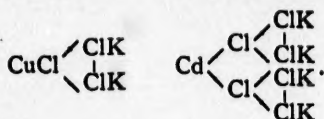
THEORETICAL.

There are now two well-established exceptions to the general law in regard to the composition of the double chlorides, namely, the salts $\text{CuCl}_2 \cdot 2\text{KCl}$ ¹ and $\text{CdCl}_2 \cdot 4\text{KCl}$ ². It is to be noticed, however, that the structure of the salt $\text{Rb}_{10}\text{Sb}_{10}\text{Cl}_{30}$ cannot be represented on the same general system as that of the ordinary double chlorides, where two chlorine atoms are supposed to be analogous in function to one oxygen atom in the oxygen salts. This statement holds true even if the formula of this chloride be somewhat simpler than that here proposed. Hence this compound is perhaps quite as exceptional as the two simpler salts mentioned. In view of these facts the author offers the following formulas as suggestions of the possible structure of these compounds. Some

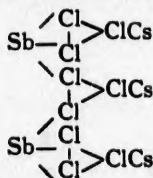
¹ Mitscherlich, Ann. chim. phys. [3] 73, 384.

² C. v. Hauer, Wien. Akad. Ber. 15, 23. These results have recently been confirmed by Dr. G. M. Richardson.

of the bonds indicated are perhaps unnecessary. They are inserted merely for the sake of representing the chlorine atoms as invariably trivalent. The essential point is the conception that a group of three chlorine atoms can have three free valencies.



According to this method of writing, the salt $\text{Cs}_3\text{Sb}_2\text{Cl}_9$ could be represented by a symmetrical formula,



By doubling the formula it could, however, be written symmetrically; according to the usual method, representing the chlorine atoms as always in pairs. By a combination of the two ideas—that a pair of chlorine atoms can have two free valencies, and that a group of three can have three free valencies—we can write a symmetrical formula for the salt $\text{Rb}_3\text{Sb}_2\text{Cl}_9$. It seems needless to give this structural formula here, as it covers a very large space. The formula of the salt $\text{Rb}_3\text{Sb}_2\text{Cl}_9$ is probably best written by representing all the chlorine atoms as united in pairs. As this is perhaps the simplest conception, an unnecessary departure from it would hardly be justifiable.

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BIOGRAPHICAL SKETCH.

Charles Edward Saunders was born at London, Ontario, February 2, 1867. After attending various schools in that city he spent four years at the University of Toronto, where he obtained the degree of Bachelor of Arts in the spring of 1888. In the same year he attended the summer school at Harvard College, and commenced his course in the Johns Hopkins University the following autumn. At the latter institution he made a special study of chemistry, mineralogy and geology, and held the position of Fellow in chemistry for the year 1890-91.